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(54) METHOD OF PREPARING ACTIVATED GRAPHITE AND CATALYSTS BASED THEREON

(71) We, ENGELHARD MINERALS & CHEMICALS CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 70 Wood Avenue South, Metro Park Plaza, Iselin, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

It has been recognized that partial oxidation of a high purity graphitized carbon may provide a useful substrate for dispersion thereon of materials such as platinum which may provide good catalytic activity. Thus in notes by M. Boudart and C.H.Bartholomew, *Journal of Catalysis*, vol. 25, pp. 173-176 (1972), a very expensive graphite channel black with a very high B.E.T. surface area of 87 m^2/g was ground to a 48 mesh powder and burned in air for about 12 hours in a muffle furnace at 600°C with a weight loss of about 50%. The resulting particles become hydrophilic and provide a support capable of adsorbing inorganic salts. For example, chloroplatinic acid with, or without, other inorganic compounds in a benzene-ethanol medium were used to provide a well dispersed platinum catalyst. However, the great loss of material during the burning tends to make such a catalyst prohibitively expensive for most applications and may cause the material to become undesirably fragile.

It is also known in the art to increase the surface area of particulate graphite material by heating graphite particles in an atmosphere of carbon dioxide at temperatures of about 1000°-1100°C. Such treatment of graphite materials with particle sizes in the range of roughly 1 to 6 mm and an initial surface area, determined by the B.E.T. gas adsorption method, of about 1 m^2/g, has been investigated. Heating at 1000°C for 1 hour may give a weight loss of about 20% and a surface area increase to only about 1.5 m^2/g, while heating for several hours has been found to increase the surface area up to about 3 m^2/g with weight losses in excess of 50%, although one test is reported to have obtained about 4.5 m^2/g with weight losses of about 30% (see for example, C.N. Spalaris, *J. Phys. Chem.*, vol. 60, pp. 1480-1483, 1956). In any event, excessive weight losses as well as severe temperature conditions and a special environment are required to obtain a surface area of about 3 m^2/g or more.

Thus only expensive treatments, involving heating in the absence of free oxygen and with great loss of the graphite during the heating, have been found effective in the past in order to increase materially the surface area of relatively inactive graphite. Graphite powders activated by the costly methods of the prior art have been found useful as supports for catalytically active metals. However, a superior activated graphite exhibiting high surface area and relatively high threshold oxidation or ignition temperatures, and catalysts based thereon, would be desirable if they could be produced economically. For such purpose the graphite starting material to be activated may be considered inactive when in particulate form, or when reduced by crushing and screening to particles suitable for surface area measurement, if its surface area is less than about 1 m^2/g. Such surface areas, referred to

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hereinbelow and in the appended claims, are measured by the conventional B.E.T. (Brunauer-Emmett-Teller) procedure or equivalent method.

Accordingly, the present invention provides a method of activating inactive graphite having a surface area of less than 1 m^2/g, which comprises:

contacting and wetting graphite having an ash content of less than 2% by weight with an organic solution of a platinum compound to deposit on the surface exposed to the solution, an amount of the solution containing at least 0.004 mg of elemental platinum per square centimeter of surface;

heating the wetted graphite with access to oxygen to remove organic solvent anddecompose the platinum compound, leaving elemental platinum disseminated on the graphite surface, heating being continued for a period of time sufficient to effect a weight loss of at least 3%, based on the weight of graphite, referred, when the graphite is in the form of a coherent or shaped body, to the weight of graphite extending 1 mm below the activated exposed surface.

In accordance with the aspect of the invention for treating a mass of low-ash graphite in the form of a coherent or shaped graphite body to activate an exposed surface of the body, the platinum compound in solution is deposited on that surface of the body, and the heating is effected with access of oxygen to that exposed surface, which then may be provided with a catalytically active material and used in carrying out catalytic reactions by passing gaseous reactants in contact with the treated exposed surface of the body.

In accordance with an advantageous aspect of the invention, a particulate mass of low-ash graphite is contacted with the platinum solution to deposit on the surfaces of the particles of the graphite mass an amount of the solution containing at least 75 ppm of elemental platinum based on the entire weight of the particles, this minimum amount of platinum being generally equivalent to the aforementioned amount of 0.004 mg per square centimeter based on the gross geometric, or superficial, or apparent area of the exposed surface or surfaces whether of a mass of graphite particles or of a eoherent body of graphite. Heating likewise is carried out to effect a loss of at least 3% of the weight of the particles. The resulting activated graphite particles may be coated with a catalytically effective amount of active catalyst material. Catalytic reactions may be effected by passing gaseous reactants through a fixed bed of the treated and coated particles.

The invention also provides an activated mass of graphite produced by a process as described above. This mass of graphite may have the form of a coherent body of graphite at least one face of which exhibits such activated surfaces. In another embodiment, the graphite has the form of a particulate mass, particles of which have activated surfaces preferably with a surface area of at least 3 m^2/g. Such particulate material will generally have disseminated thereon between 75 and 2000 ppm of elemental platinum based on the weight of the particles.

In accordance with a method feature of the invention, a carbonaceous material is oxidized by contacting the material in gaseous form under oxidizing conditions with a catalyst in the form of a mass of graphite -- which may be a coherent body of graphite with an activated surface or a mass of particulate graphite material the particles of which have activated surfaces -- such surfaces being activated by heating in the presence of elemental platinum disseminated on those surfaces with substantial burning off of graphite from those surfaces, the mass of graphite also having incorporated to its activated surfaces a catalytically effective amount of a catalyst material. Gaseous fuel-air mixtures, in particular utilizing lower alkane carbonaceous fuels, advantageously are oxidized or combusted by contacting with such activated graphite surfaces carrying a catalytically effective amount of at least one platinum group metal.

Figure 1 is a diagrammatic representation in vertical cross-section of a catalytic burner utilizing particulate graphite catalyst materials prepared in accordance with the present invention.

Figure 2 is a diagrammatic representation in vertical cross-section of a catalytic burner utilizing a shaped, coherent graphite catalyst body prepared in accordance with the present invention.

Graphite is a crystalline form of carbon which not only occurs naturally but also is produced synthetically in large quantities. Synthetic graphite is manufactured by heating carbonaceous materials such as petroleum coke in the range of 900°C to 1800°C to form an amorphous carbon, followed by further heating at temperatures between 2200°C to 3000°C to transform the amorphous carbon to the crystalline form. While it might be possible to utilize certain forms of natural graphite, depending upon the crystalline structure and purity, the present invention principally involves the use of artificial or synthetic graphite.

Synthetic graphite is commercially avalable in a wide diversity of purities, which may be expressed as ash content. The ash content of graphite is the percentage residue obtained when a sample is ignited under an abundance of air at 900°C or higher to constant weight.

ordinarily for about an hour or more. In general, the ash content of most synthetic graphites varies from essentially 0% to 5% by weight. The ash portion generally contains one or more of the elements silicon, calcium, ir n, aluminum, titanium, vanadium, sodium, boron, and sulfur. In addition the ash may contai small or trace amounts of barium, beryllium, bismuth, chromium, cobalt, zirconium, lead, manganese, molybdenum, nickel, strontium, tin, tungsten, zinc, niobium, tantalum, and uranium. It is especially noteworthy that commercial graphites are free of even trace amounts of platinum.

Graphite is a widely available commercial material in physical forms such as powders, granules, extruded and molded shapes, and manufactures and structures of a wide variety, all of which find extensive application in the metallurgical, chemical, nuclear, and aerospace industries.

The application of graphites and graphite structures and shapes in the field of catalysis is limited and poorly developed compared to the use of amorphous carbon. This limited use of graphite may be attributed to the presence of the aforementioned impurities, many of which are capable the of catalytic action in either a positive or negative sense, and some interfere with the catalytic action of a desired metal deposited on the graphite as a catalytic agent. Whereas low-ash graphites are sold in commerce and would be expected to be more suitable as a catalyst support than the high-ash grades, the low-ash and relatively pure graphites, that is graphites with an ash content of a maximum of 2%, are conventionally produced by graphitization at extremely high temperatures, generally in the range of 3000°C, to decompose and volatilize most of the impurities contained in the carbon. As the result of this high temperature treatment, most commercially particulate low-ash synthetic graphites presently available, such as plates, granules, and pellets have a surface area of less than one square meter per gram (m^2/g). To provide a material suitable for many applications to catalytic reactions, this surface area is too low to permit impregnation of the plate surfaces or of the particles with adequate amounts of catalytically active metals in available form. Thus these graphites may be termed inactive.

The catalyzed and non-catalyzed oxidation and gasification of graphite by molecular or atomic oxygen, dry and damp air, ozone and carbon dioxide was extensively studied by P.L. Walker and co-worker. Their work is reported extensively in "Chemistry and Physics of Carbon", Walker & Thrower, Eds., volumes I-XI, Marcel Dekker, Inc., New York, 1966-1973. The scope of Walker's work was to clarify the mechanisms of oxidation and gasification reactions of graphite by microscopic and cinematographic studies of the oxidation reaction. The effect of catalysts such as silver, gold, barium, boron, beryllium, calcium, chromium, cadmium, cobalt, copper, iron, potassium, molybdenum, manganese, sodium, nickel, lead, scandium, strontium, tantalum, tellurium, titanium, vanadium, and zinc was examined and differences in oxidation attack in certain crystallographic directions of the graphite was demonstrated. The surface topography and its change during oxidation and gasification was the major object of the study. So far as can be ascertained, no practical process for catalyst manufacture was indicated in the Walker work, nor do Walker et al. describe graphite materials suitable for most uses as the catalytic materials required by current technology. It is noteworthy that these extensive and authoritative studies did not investigate the effect of platinum.

In many respects, graphite might be considered as a highly desirable catalyst support. It possesses excellent corrosion resistance to acids, alkalies, and organic and inorganic compounds. In addition, the low-ash graphites are more resistant against oxidation by air or oxygen than is amorphous carbon, suggesting the use of such materials as catalyst supports for combustion and oxidation reactions. Further, graphite has excellent mechanical strength, and is a good heat conductor making it useful for applicaton in fixed bed chemical reactors where good dissipation of reaction heat is a requirement.

The deposition of metals or compounds on graphite is generally known. Such techniques, however, tend to be cumbersome or often do not result in a uniform dispersion of metals. Among such prior art methods are: evaporation of metals onto graphite using high-vacuum sputtering techniques; impregnation of graphite with molten metals such as silver; preparation of colloidal metal suspensions by electro-mechnical methods and deposition of the metal colloids on the graphite; decomposition of metal carbonyls into fine metal powder and applying or mixing the metal powder with graphite; impregnation of graphite with aqueous solutions of inorganic salts such as shown in U.S. patent No. 3,759,842, issued September 18, 1973, to Bianchi et al.; impregnation of non-catalyzed preburned graphite with a solution of hexachloroplatinic acid and ferric nitrate in a mixture of methanol and benzene as described by Boudart et al. in *J. of Catalysis*, mentioned hereinabove, and the impregnation of carbon and graphite with ruthenium acetylacetonate solutions as described in U.S. patent No. 3,850,668, issued November 26, 1974 to Heffer.

It is recognized that organic solvents wet the hydrophobic surface of graphite. For obtaining a coating of a metal-containing compound on graphite it thus would be desirable

to treat the graphite with a solution of the metal-containing compound in an organic solvent formulation to provide an adherent film of the coating solution containing the metal. It will be helpful to discuss several types of platinum compounds useful in carrying out the present invention which are available to the art and which are soluble in organic solvents. Some of the materials discussed have been available for applying to surfaces to provide decorative coatings, or for such applications as the formation of reflective, conductive, or other films for electronic or instrumentation use.

So-called platinum resinates may be used advantageously in carrying out the present invention, and their provision will be discussed first. Turpentine typically is a mixture of bicyclic terpenes such as pinene, monocyclic terpenes such as terpinene, abietic acid (cyclic diterpene resin acid), and abietic anhydride. Balsam typically is a somewhat less volatile mixture rich in terpenes and various deterpene resin acids, and may contain sesquiterpenes such as caryophyllene; cinnamic and benzoic acids or nonresinous esters thereof need not be present for the use to be described. Procedures for sulfurization of such mixtures have been long known in the art. Thus P. Boudnikoff set forth (Compt. Rend. 196, pp. 1898-9, 1933) the preparation of a sulfurized product, designated terpene sulfide, by boiling a mixture of Venetian turpentine with sulfur flowers or nitrogen sulfide, N_4S_4, for one and a half hours at 160°-170°C. The terpene sulfide product may be reacted with auric chloride or with potassium tetrachloro-aurate to produce gold resinate. F. Chemnitius had described (Sprechsaal 60, p. 226, 1927) the preparation of a platinum-containing resin soluble in essential oils or other vehicles, by reacting sulfurized balsam in alcoholic solution with a platinum salt (specifically hexachloroplatinic acid), distilling off the alcohol, and purifying to obtain a solid product. Related resin, resin acid, and terpene materials and mixtures may be sulfurized similarly; the resulting sulfurized terpene or sulfurized resin likewise may be reacted with a platinum salt to obtain a soluble platinum-containing material known in the art as a platinum sulforesinate or simply platinum resinate, as referred to in U.S. patent No. 3,022,177, and similarly in patent No. 3,092,504 (e.g., Example XII thereof), which are incorporated herein by reference. Similar procedures are referred to in patents No. 2,402,698 and 2,407,265 which describe the formation of sulfurized terpene compounds or terpene-sulfur complexes from 2-pinene (apha-pinene), 2(10)-pinene (beta-pinene), p-mentha-1,8-diene (dipentene), p-mentha-1,4(8)-diene (terpinolene), p-menth-3-ene (menthene), p-menth-1-en-8-ol (alpha-terpineol), camphene (3,3-dimethyl-2-methylenenorbornane), and mixtures of terpenes such as are found in turpentine. These sulfurized terpenes were obtained by reacting the terpenes with equimolar or higher proportions of sulfur at about 150 C for 8 hours or longer under autogenous pressure, and illustrate the variety of terpenes and related materials which can be sulfurized separately or in mixtures of the types found in turpentine and balsam. The patents referred to above as showing the formation of sulforesinates utilize the sulforesinates in the preparation of resinates of various metals which may be used in decorating compositions, or as intermediates in the preparation of thiols (mercaptans) and of further derivatives thereof which may contain precious metals.

As mentioned above, platinum resinate may be dissolved in essential oils or other nonvolatile organic vehicles such as oils of lavender, rosemary, aniseed, sassafras, wintergreen, and fennel, which may contain also more volatile solvents or thinners such as turpentine and nitrobenzene. The solution so formulated, with or without other film-forming ingredients, may be applied to various substrates to obtain a coating containing the platinum resinate. For example, after application in a thermoplastic medium to refractory substrates such as glass, ceramic, and stainless steel, the coating containing platinum resinate or mixtures of various metal resinates may be fired to obtain highly decorative precious metal finishes (patent No. 3,092,504). A typical platinum resinate solution in an essential oil vehicle contains 12% metallic platinum by weight. Solutions in such largely nonvolatile organic vehicles of resinates of other precious metals and of base metals likewise are available.

Another class of platinum-containing compounds which may be dissolved in organic solvents to provide coating compositions as high or higher in platinum is disclosed in the aforementioned U.S. patent No. 3,022,177 of H.M. Fitch. These compounds are soluble halogenoplatinous mercaptide-sulfide compounds. Such compounds also may be designated soluble halogeno(alkylthio)platinum(II) complexes with alkyl sulfides in which the alkyl groups may be modified, as indicated by the formula R-S-Pt-X.Y in which the R is selected from the group consisting of alkyl, substituted alkyl, aralkyl, and terpenyl, X is halogen, and Y is selected from the group consisting of alkyl sulfides, substituted alkyl sulfides, and heterocyclic sulfides containing a $-CH_2SCH_2-$ linkage in the ring, the two alkyl or modified alkyl groups together containing at least seven carbon atoms.

Illustrative of the soluble halogenoplatinous mercaptide-sulfide complexes are the following, in which the alkyl groups in both mercaptide and sulfide moieties are not

substituted or otherwise modified:

Chloro(tert-heptylthio)platinum(II)-butyl sulfide
Chloro(octylthio)platinum(II)-ethyl sulfide

In the following complex the mercaptide moiety has a cyclic terpenyl group, representative of such groups utilized in forming terpenethiols by sulfurizing terpenes (as present in turpentine and balsam) followed by hydrogenation:

Chloro(pinenethio)platinum(II)-methyl sulfide, or
Chloro(pinanylthio)platinum(II)-methyl sulfide,

the latter designation indicating that some or all of the terpene moiety becomes saturated during the formation of the terpenyl mercaptan (pinene mercaptan), which then is reacted with potassium tetrachloroplatinate(II) and methyl sulfide to form the complex.

A complex having good solubility and including a substituted-alkylthio group is the compound with methyl sulfide of the isooctyl ester of [(carboxymethyl)thio]chloroplatinum(II), the mercaptide moiety alternatively being named chloroplatinous isooctyloxycarbonylmethyl mercaptide.

The following complex includes an aralkylthio group in the mercaptide moiety:

Chloro[(alpha-methylbenzyl)thio]platinum(II)-ethyl sulfide

Variants of the first-mentioned mercaptide-butyl sulfide complex, in which the mercaptide moiety may be designated chloroplatinous tert-heptyl mercaptide, are illustrated by the following complexes with ethylmercaptoethanol, which is a substituted alkyl sulfide, or with tetrahydrothiophene, a heterocyclic sulfide:

Chloro(tert-heptylthio)platinum(II)-2-(ethylthio) ethanol
Chloro(tert-heptylthio)platinum(II)-tetrahydrothiophene

Another platinum compound moderately soluble in organic solvents is dibromobis (glycine) platinum (II), $[PtBr_2(NH_2CH_2\text{-}COOH)_2]$, and the corresponding dichloro or diiodo complex also may be used. As a further example, better solubility in appropriate organic solvents can be expected with another diamine complex, dichlorobis(aniline)platinum(II), $[PtCl_2(C_6H_5NH_2)_2]$.

Illustrative of another type of soluble platinum compounds is the etherate of platinum (IV) chloride with isopropyl ether, $PtCl_4.O[CH(CH_3)_2]_2$.

Another useful platinum (IV) complex is platinic acid (hexahydroxyplatinic acid), $H_2Pt(OH)_6$, which is readily soluble in an aqueous organic solvent medium including a nonvolatile organic solvent such as 2-aminoethanol or 2,2'-iminodiethanol. Thus, dissolving 27.6 kg of platinic acid in a mixture of 2-aminoethanol (8.3 kg) and water (43.6 kg) gives a 22.6% solution by weight of platinum.

While the theoretical mechanism by which improvement is obtained in the surface area and in other criteria of activation of the graphite is not of itself a part of the present invention, it is believed that such improvement is realized through the catalytic activity of small amounts of elemental platinum which are provided on the exposed surfaces of the graphite during the burning or oxidation treatment. Ordinarily the platinum is disseminated on the graphite to be activated in amounts of 75 to 2000 ppm by weight of graphite particles, or over 0.004 and conveniently 0.02 or more mg per square centimeter of graphite plate surfaces. The platinum remains stable in elemental form in the presence of oxygen and retains its catalytic activity in effecting the desired selective oxidation at localized sites, thus preparing the graphite surfaces at elevated temperatures (generally below 900°C) and for short treatment times in the presence of oxygen, resulting in minimal loss of weight of the graphite. The presence of the platinum is believed to facilitate the formation of the minute etch pits or pores which provide the desirably high effective surface area. During the initial heating, the volatile solvents are driven off, followed by evaporation or decomposition of some or all of the nonvolatile solvents, thus removing the solvent medium. As the heating progresses, the compound or complex containing the platinum is decomposed, along with the film-formers and any remaining organic ingredients of the coating composition, leaving the platinum metal in a desirable state of dissemination, which may be quite sparse, on the graphite surfaces. Further heating in the presence of oxygen, ordinarily the oxygen of the ambient air, effects oxidation of a moderate amount of the graphite carbon, and the development of a higher surface area is believed to be effected by preferential oxidation under the influence of, and in the neighborhood of, the minute platinum deposits.

Generally the presence of the platinum, disseminated on the surfaces being heated, facilitates oxidation, causing a loss of weight by burning off of some of the graphite on and near the surfaces. Although this loss of weight may be in only small proportions, it still is substantially greater than the loss would be if untreated material were heated for the same periods of time at the same temperature, unless the temperature is quite elevated.

The following examples are intended to illustrate the present invention and point out the presently preferred embodiments thereof, but without limiting the scope of the invention as it may be understood in its broad aspects by one skilled in the art in view of the discussion and explanations herein.

Example 1

The graphite material used was a granular graphite (Union Carbide Corp., grade BB-6) containing about 75% by weight of particle size −10+20 mesh in the Tyler sieve series, about 18% larger than 10 mesh most of which by weight passed the 8 mesh screen, and the remainder passing the 20 mesh screen. The material was rescreened to −8+16 mesh to remove oversize particles and powders. This left a particulate material substantially free of powdered fines in which the particles have diameters (in the substantial absence of particles of acicular shape) predominantly in the range of 1 mm to 5 mm, i.e., of the order of 2 mm, and more specifically having diameters predominantly in the range of 1 mm to 2.5 mm. The ash content of the graphite material was less than 2% by weight and generally substantially less, in the region of 1-1.3%.

The soluble platinum compound chosen for coating the graphite particles was platinum resinate (platinum sulforesinate), made of sulfurized balsam reacted with a platinum salt, dissolved in a mixture of nonvolatile essential oils. 14 grams of this solution contaning 12% platinum metal by weight (1.68 grams platinum) were mixed with gilsonite (10 grams), benzene (250 grams), and toluene (50 grams), the benzene and toluene being volatile solvents added to decrease the viscosity, improve the ability of the solution to wet graphite surfaces, and permit application of a weaker solution. The gilsonite, providing a viscous asphaltic film-former, first was dissolved under stirring in warm benzene and then the resinate solution and toluene added under stirring. The final solution was stored in a glass bottle with stopper.

A total of 1836 grams of graphite was impregnated in 100 gram portions by placing about 100 grams of the granules in a separatory funnel in upright position and pouring the solution onto the mass of graphite particles until completely covered with the liquid. After five minutes holding time, the excess solution was drained off and returned to the glass bottle for reuse. The wet coated graphite in a glass dish was placed in a fume hood to allow evaporation of volatile solvents under ambient conditions. This procedure was repeated with successive portions of the graphite, the total amount of which required 277 grams of the solution containing 1.43 grams platinum in the platinum resinate. The calculated platinum loading of the graphite corresponded to 780 ppm platinum metal.

The dried and coated graphite was placed on ceramic trays in layers about 0.6 to 1.2 cm thick and the trays slowly moved into an electric muffle furnace preheated to 600°C. Decomposition of the resinate coating to leaving the desired minute platinum metal deposits disseminated on the graphite surfaces occurs quite rapidly as temperatures approaching about 300°C are reached, resulting in evolution of fumes, and the furnace door then was closed and an oxidizing atmosphere maintained in the furnace by continuously purging air into the furnace through a 0.6 cm ceramic tube. Each hour the graphite granules in each tray were shaken to permit granules at the bottom of the tray to come to the surface of the layer. After 3 hours at 600°C, the weight loss of the graphite was about 18% and its surface area had increased from less than 1 m^2/g to 6.2 m^2/g. It will be understood that atmospheric oxygen conveniently is used to effect oxidation during the heating, but that other sources of gaseous oxygen may be used.

In this procedure a muffle furnace was conveniently available for use. Alternatively a tunnel furnace may be used advantageously, the coated graphite being passed through the furnace in thin layers on a conveyor. Also advantageous for use in this heating procedure would be a continuous rotary calciner, in which the heating required for carrying out the method of the present invention may be effected while maintaning the furnace at a temperature in the range of 600° to 800°C with the coated graphite particles passing through the furnace usually in less than one hour. However, when the heating is carried out so as to raise the temperature of the surface portions of the coated particles rather quickly, care should be taken to allow a sufficient residence time, say at least 10-20 minutes, while the surface temperatures rise to about 300°C so as to avoid too rapid burning of the coating and to permit orderly evolution and disposition of the solvents and decomposition products of organic material in the coatings.

For the soluble platinum compound used in the example just described there may be

substituted with equivalent results a halogenoplatinous mercaptide-sulfide complex containing the same weight of platinum metal. Thus as a similar example the isooctyl ester of [(carboxymethyl)thio]chloroplatinum(II) complexed with methyl sulfide is used in a toluene solution containing about 25% platinum by weight, with which is included as the solvent vehicle essential oils, turpentine oil, and gilsonite in benzene solution for application to form a suitable platinum-containing film on the graphite particles with care to obtain uniform dispersion on the graphite surfaces. After evaporation of some of the more volatile solvents, the heating step is commenced and the coated film is burned off with decomposition of the mercaptide-sulfide complex to leave the elemental platinum on the graphite surfaces, followed by heating at 600°C as described above.

Example 2

Numerous runs were carried out, and the results are summarized in Table I and II below, to illustrate the effects of reaction variables such as oxidation time (heating time in hours), oxidation temperatjre (heating temperature in degrees C), the type and amount of elemental previous metal in the coating (ppm metal derived from the coating solution used, based on original weight of graphite). weight loss of the graphite based on its original weight (percent loss), and the specific surface area of the product in m^2/g as determined by the standardized B.E.T. procedure. Weight losses are reported for the successful runs of between about 3% and about 40% of the weight of graphite particles being treated, while in one case slightly over half of the weight was lost. In these experiments the preparation of solutions of previous metal resinate. the coating of the graphite, and the burning or oxidation were carried out as described in Example 1.

Referring to Table I, however. runs Nos. 1-12 were made with only the heating step, using uncoated graphite particles. It may be seen from these runs that the uncoated graphite, whose surface area was measured at 0.9 m^2/g before heating,

TABLE I

Run No.	*Metal in Coating*	*Metal Weight, ppm*	*Heating Time, hrs.*	*Heating Temp., °C*	*Weight Loss, %*	*Surface Area m^2/g*
1	None		None		None	0.9
2	"		1	550	1.1	0.9
3	"		1	600	1.8	1.3
4	"		0.5	700	5.7	1.5
5	"		1	700	11.7	1.7
6	"		2	700	22.1	2.0
7	"		3	700	31.4	2.3
8	"		4	700	39.7	2.4
9	"		5	700	48.4	2.7
10	"		5.5	700	53.1	2.8
11	"		6.5	700	62.2	2.7
12	"		1.5	850	15.0	1.0
13	Pt/Ag	390/400	3	600	22.8	2.7
14	Pt/Ag	260/530	3	600	26.1	3.0
15	Ag	680	3.5	600	31.0	3.0
16	Au	785	3	600	4.5	1.8
17	Ir	715	3	600	4.0	2.0
18	Ir	715	5	600	6.0	2.2
19	Pd	920	3	600	4.5	1.8
20	Pd	920	23	600	28.2	2.6
21	Pd	1120	4	600	5.5	1.8
22	Rh	790	3	600	6.2	2.3
23	Ru	1185	3	600	5.8	3.2

TABLE II

Run No.	Metal in Coating	Metal Weight, ppm	Heating Time, hrs.	Heating Temp., °C	Weight Loss %	Surface Area m^2/g
24	Pt	152	5	600	9.6	4.8
25	Pt	152	0.9	750	17.4	3.3
26	Pt	382	1.3	600	3.3	3.2
27	Pt	382	3	600	10.3	5.0
28	Pt	382	4.5	600	17.5	6.1
29	Pt	760	3	600	16.5	6.0
30	Pt	780	3	600	18.0	6.2
31	Pt	1610	1.2	525	3.0	1.8
32	Pt	1610	3.2	525	3.7	2.6
33	Pt	1610	23	525	13.2	3.3
34	Pt	1740	1.3	600	14.8	6.0
35	Pt	1740	3	600	33.3	7.0
36	Pt	1740	4.7	600	38.4	7.3
37	Pt	132	4	600	6.3	4.4
38	Pt	340	2.5	550	8.3	5.7
39	Pt	340	3	600	53.0	9.0

could not be improved to have a surface area over, say, 3 m^2/g even when heated in the presence of air at temperatures as high as 850°C or for periods of time exceeding six hours, and even though runs Nos. 10 and 11 carried out at 700°C caused graphite weight losses well in excess of 50%. Additional runs which used graphite particles coated with precious metals other than, or in addition to, platinum also are listed in Table I and will be discussed hereinbelow.

With platinum disseminated on the graphite surfaces, however, surface areas of at least about 3 m^2/g were obtained readily with reasonable weight losses. Illustrative examples are listed in Table II. Thus in runs Nos. 24 to 30 surface areas of 3.2 to 6.2 m^2/g were obtained with moderate weight losses at a furnace temperature (except run No. 25) of 600°C, and the preferred operation is emplified by these runs (except runs Nos. 25 and 26 in which heating was continued for less than an hour and for only 1-1/3 hours respectively) with weight losses within a range of about 6% to 25% to provide a surface area of at least about 4 m^2/g. The results of Example 1 are reported in Table II as run No. 30.

In run No. 25, the effect of increasing the heating temperature was investigated. This run was comparable to run No. 24, using the same amount of platinum, but the temperature was increased from 600° to 750°C and heating was continued for a much shorter time of 0.9 hour. Although the weight loss was about the same as that encountered in run No. 28, which used more disseminated platinum with heating for 4.5 hours at 600°C, the surface area in run No. 25 reached only 3.3 instead of 6.1 m^2/g. The reason for the lower surface area with comparable weight loss in run No. 25 is not certain. It may be speculated nevertheless that catalytic burning and etching, occurring selectively at localized sites, preponderates at heating temperatures above about 500°C and up to well over 600°C. However, as temperatures are advanced into the 700°-800°C range, it is possible that random thermal oxidation over the entire surface tends to increase at the higher temperatures and begins to override localized catalytic oxidation with its etching effect, so that similar weight losses may become associated with decreasing net surface area. In any

event, a comparison of runs Nos. 12 and 25 indicates that, when disseminated platinum is present, the heating temperatures and time may be adjusted to obtain quite beneficial improvements in surface area for a given weight loss with minimal heating time.

For a further comparison with runs Nos. 12, 24, and 25, and again using 152 ppm platinum, the particulate graphite was heated at a still higher temperature of 850°C for only somewhat over half an hour to obtain closely the same weight loss as that encountered in run No. 25. Under these conditions, however, while the surface area increased considerably, it still did not quite reach 3 m^2/g. This might be explained by assuming that a random thermal burning was masking still further the localised etching effects attributed to catalytic oxidation. It appears that heating temperatures in the range of about 500°-800°C, with suitable adjustment of the amount of platinum used and the time of heating in correlation with the specific temperature, can provide an optimum balance between weight loss and increase in surface area. Within limited ranges of platinum loading and temperature, a shorter heating period may be offset by a higher heating temperature for given approximate weight loss and surface area obtained. As already suggested, it may be possible to effect the heating quickly and at relatively high temperatures in suitable furnace equipment, in which temperatures above 800°C could be held for relatively short periods of time without excessive weight loss to achieve high surface areas. Those skilled in the art will appreciate that different graphite materials may have different microscopic structures, depending on their source and mode of production and possibly on the inclusion of binders or other constituents as in molded graphite shapes. These differences could affect the results of heating, which also is affected to some degree, of course, by the readiness of access of air or oxygen to the graphite surfaces, whether the graphite is in coherent or particulate form. The optimum temperature also may be affected by factors such as the particular structure of the furnace and feeding apparatus and the disposition of the graphite mass during heating, as well as the detailed temperature-time program of the heating. Thus the determination of the maximum or preferred temperature must be left to the ordinary skill of the art, aided by the discussion herein, and may require some routine experimentation for a given material and furnace installation and in view of the characteristics desired for the activated graphite. In any event, it appears from the data presented herewith that many graphite materials can be heated to at least 850° to 900°C for short periods of time without uncontrolled burning or ignition, even in the presence of platinum disseminated on the surfaces.

Referring further to Table II, in runs Nos. 31 and 32 the furnace temperature was lowered to 525°C and the heating time was too short to obtain a threefold increase in surface area in spite of a higher deposition of platinum. Run No. 33, carried out at the same temperature, effected substantial improvement in the surface area with reasonable weight loss, but the heating had to be carried out for almost a full day to obtain these results. A relatively high platinum loading of 1610 ppm was used in all three runs.

A still higher platinum loading of 1740 ppm was used in runs Nos. 34 to 36 to illustrate the lower heating time which may be suitable at 600°C with the greater amounts of platinum. Thus in run No. 34 a surface area of 6 m^2/g was obtained in only 1-1/3 hours with a weight loss of less than 15%. Even higher surface areas were obtained in runs Nos. 35 and 36 in heating times of 3-5 hours, but with greater weight losses of up to about 40%. However, such weight losses in the range of 5%-40% and specifically in the neighborhood of 25%-40% may be appropriate for some applications, for example when the graphite used is relatively inexpensive and the resulting activated graphite is particularly suited for a specialized end use, and especially when surface areas of 7 m^2/g or higher are achieved. Runs Nos. 28-30 and 34-36 nevertheless show that, when a loss of at least about 10% of the weight of the graphite particles is acceptable, a surface area of at least about 6 m^2/g can be attained.

Other examples shown in Table II, including runs Nos. 37 and 38 in which weight losses of somewhat over 6% gave surface areas over 4 m^2/g, and run No. 39 in which a weight loss much greater than 10% was tolerated to provide a surface area much higher than 6 m^2/g, will be described hereinbelow. It may be noted here, furthermore, that run No. 38, which used a different particulate graphite material and 340 ppm platinum, was able to produce a similar weight loss and a somewhat higher surface area in 2.5 hours at 550°C than were produced by run No. 27 in 3 hours at 600°C with a similar platinum loading of 382 ppm.

Regarding heating at temperatures below about 600°C, the particulate material used in runs Nos. 24-36 appears from run No. 33 to require a temperature of about 500°C or higher to achieve the desired minimum surface area in a practical period of heating, although runs Nos. 34-36 suggest that an increase of platinum loading to above 1700 ppm and even as high as 2000 ppm would permit attainment of a surface area greater than 3 m^2/g in a relatively short time at a temperature of 525°C or somewhat lower. It appears that there are other inactive graphite materials, such as used in run No. 38, which are suitable for heating at

temperatures in the range of about 500°-550°C with rather low platinum loadings and for periods of several hours or more to obtain acceptably high surface areas. Thus a temperature of about 500° to 800°C is preferred for the heating operation.

It should be pointed out, however, that use of air at standard atmospheric pressure provides a partial pressure of oxygen of only slightly above 0.2 atmosphere. It will be understood by those skilled in the art, that the oxidation, which is achieved during the heating in the neighborhood of the platinum disposed on the graphite surfaces, will be accelerated at a given temperature by increasing the partial pressure of oxygen available at the graphite surfaces. This may be done, for example, by adding some pure oxygen to the air admitted to the graphite body during the heating. For many heating procedures the effective concentration of oxygen at the graphite surface is increased more conveniently by pressurizing the equipment. Thus air at a pressure of 2 atmospheres will have an oxygen partial pressure of about 0.4 atmosphere, while dry air pressure need be increased to only 5 atmospheres to raise the partial pressure of oxygen to over 760 mm Hg (1 atmosphere). It will be understood further that such increases in the partial pressure of oxygen will cause corresponding increases in the weight loss and surface area, when a given graphite material with a given amount of platinum disseminated on its surfaces is heated at predetermined temperatures for predetermined periods of time.

Accordingly, the heating may be carried out at elevated but lower temperatures, which may be substantially below 500°C as dictated by the reaction kinetics, to obtain a desired increase in surface area in a period of several hours, or even less than an hour, by using higher concentrations of oxygen or using air under substantial pressure. Care must be taken, of course, to avoid excessive or uncontrolled burning or even ignition of the graphite, by limiting the temperature to which the material is heated in view of the partial pressure of the available oxygen.

In run No. 37, the effect of heating at 600°C was determined using somewhat larger graphite particles with a relatively small amount of platinum disseminated thereon. The graphite as supplied (Union Carbide Corp., grade BB-7) was found to have the following approximate particle size distribution by weight: −3+4 mesh, 57%; −4+8 mesh, 42%; with approximately 1% passing the 8 mesh screen. Only the fraction passing the 4 mesh screen but larger than 8 mesh was used, providing a particulate material substantially free of powders and of oversized particles, and having diameters predominantly in the range of 1 mm to 5 mm and, more specifically, predominantly in the range of 2.5 to 5 mm. This −4+8 mesh fraction before treatment also had an effective surface area by B.E.T. measurement of about 0.9m²/g. After heating 4 hours at 600°C with a platinum loading of 132 ppm and a weight loss of 6.3% the surface area had increased to 4.4 m²/g, quite similarly to run No. 24 using the smaller particles.

Runs Nos. 38 and 39 using another graphite particulate material will be discussed hereinbelow in connection with Example 6.

Each of runs Nos. 24-30 and 33-39 produced a mass of graphite in the form of a particulate mass, having surfaces activated by heating the mass in the presence of elemental platinum disseminated on the surfaces with substantial burning off of graphite from the surfaces and with the platinum remaining disseminated thereon. The particulate graphite material, with particle diameters predominantly in the range of 1 mm to 5 mm, had a surface area of at least about 3 m²/g, and had disseminated on the particles thereof between 75 and 2000 ppm of elemental graphite.

The effects of other precious metals, including use of a coating containing a silver resinate as well as a platinum resinate, are indicated in runs Nos. 13 to 23 reported in Table 1. In only three of these runs did the surface area reach 3 m²/g, and in runs Nos. 14 (platinum and silver) and 15 (silver) the weight losses exceeded 25% with only marginally desirable improvements in surface area. Runs Nos. 16 to 18 used gold or iridium in substantial proportions with small improvement in surface area after 3-5 hours of heating at 600°C. Palladium was tried in runs Nos. 19 to 21, resulting in a surface area of only 2.6 m²/g after 23 hours of heating at 600°C with a weight loss of 28.2%. It is probable that the palladium deposits become oxidized as the heating time and temperature together reach a level sufficient to obtain a substantial amount of oxidation, and that the oxidized palladium does not function suitably as a catalyst in obtaining a desirable preferential oxidation. Run No. 22 using rhodium at the same heating temperature also produced a mediocre improvement in surface area. Run No. 23 used ruthenium in relatively high proportion and produced an acceptable improvement in surface area, but this run may be compared with run No. 27, using less than a third as much platinum by weight and the same heating time and temperature to give a surface area of 5 m²/g and still with a moderate weight loss.

Examples 3-5 relate to the preparation of granular catalysts utilizing graphite substrates. A great variety of procedures and materials is available to the art for obtaining catalysts utilizing catalytically active precious metals and base metals on substrates of suitably high

surface area, the choice of type and concentration of materials depending on the reaction to be catalyzed under predetermined conditions and on economic factors, as is well understood by those skilled in catalysis. Several illustrative examples are given hereinbelow.

Example 3

This example illustrates the preparation of a granular platinum-graphite catalyst, containing nominally 0.88% (8800 ppm) platinum by weight. The activated graphite catalyst support was prepared as described in Example 1, and possessed a specific surface area of 6 m^2/g.

The graphite support (427 grams) was placed in a laboratory-size glass coating pan. Platinum resinate dissolved in an essential oil vehicle as described above (31.8 grams at 12% platinum) was mixed with benzene (146 grams) and toluene (30 grams), and the resulting solution was poured onto the graphite in a rotating coating pan. After mixing for one minute, the coated and wet graphite was transferred to a glass dish in a fume hood. The granules were stirred occasionally with a spatula to expedite evaporation of solvents. The impregnated graphite was then further dried in a mechanical convection oven at 100°C for 30 minutes. The temperature in the oven then was raised to 300°C in 90 minutes, and the granules were held at this temperature for 30 minutes to decompose the resinate and evaporate solvent without weight loss of the graphite. The oven then was cooled at 100°C and the catalyst bottled.

It may be noted that the platinum utilized in preparing the activated graphite remains on the graphite in small amounts. Unless this platinum is removed, as by acid leaching in known manner, it contributes in small or trace amounts to the platinum or other catalyst metals which may be subsequently incorporated on the catalyst as in these examples.

Example 4

This example illustrates the preparation of a bimetallic noble metal catalyst utilizing a graphite substrate. The nominal metal content of the finished catalyst (in addition to the very much smaller proportion of platinum used in the activating treatment) was 1.8% palladium and 0.79% gold by weight. The support used was granular graphite (from Union Carbide Corp., grade BB-7) prepared as indicated in Example 2 under run No. 37 (Table II), with selective oxidation at 600°C using 132 ppm of platinum disseminated on the graphite particles, to attain a surface area of 4.4 m^2/g.

The graphite support (562 grams) was placed in a laboratory-size glass coating pan. A gold resinate dissolved in a mixture of essential oils (38.1 grams at 12% gold) and a similar palladium resinate solution (116.4 grams at 9% palladium) were dissolved together in toluene (100 grams). The resulting solution was poured onto the graphite contained in the rotating coating pan, mixed for one minute, and subsequently the rotating pan plus contents were heated by positioning a heat lamp above the pan. Heating was continued until a tacky granular mass was obtained. The coated granules were transferred to a ceramic tray. The granules in the tray were dried in a mechanical convection oven for 15 minutes at 100°C, heated to 300°C in 60 minutes, kept at 300°C for 60 minutes, then cooled down to ambient temperature, and the catalyst then was bottled.

Example 5

This example illustrates the preparation of a base metal catalyst on activated granular graphite. The nominal metal content of the catalyst was 1.0% iron. The particulate activated graphite support (198 grams) was placed in a laboratory-size coating pan. An iron resinate solution (16.8 grams at 11.9% iron) was dissolved in toluene (50 grams). The resulting solution was poured onto the graphite in the rotating pan, mixed for one minute, and the mixture in the pan heated with heat lamps to evaporate the toluene. The granular mass was then transferred to a ceramic tray in a mechanical convection oven. The oven was heated to 350°C in 60 minutes and maintained at 350°C for 30 minutes, and the tray then was removed from the oven. After cooling, the catalyst was bottled.

Example 6

Another graphite material was tested for use either in particulate form or as a body or plate in nonparticulate (that is, coherent) form. This graphite material is available in the trade as molded rectangular blocks 15 cm × 15 cm × 5 cm thick (Pure Carbon Company, Inc., St. Marys, Pa., grade FC-36). This material is reported to have a low-ash content of about 0.1% by weight and a specific surface area of as little as 0.3 m^2/g indicating that the material is very inactive. To confirm the suitability of this material either in particulate or coherent form for activation in accordance with the present invention, a block of the material was crushed and reduced in size of mortaring; upon screening, a fraction was

obtained of −8+14 mesh, thus providing a particulate material, the particles of which had diameters predominantly in the range of 1 mm to 5 mm, comparable to the dimensions of the particles used in the runs described in Examples 1 and 2.

The surface area of the particles thus obtained by mortaring and screening was determined by B.E.T. measurement to be 0.4 m^2/g. A mass of these uncoated particles having a shiny, dark appearance was subjected to a temperature of 600°C for 3 hours in the presence of air. Subsequent measurement of the weight and activity of the mass of particles so treated showed a weight loss of 5.5% and a surface area of 1.4 m^2/g. The results of this test may be compared with runs Nos. 1-4 reported in Example 2 and in Table I.

For testing the effect of heating this graphite material when carrying elemental platinum on its exposed surfaces, a platinum resinate-gilsonite solution in benzene and toluene was prepared as in Example 1 utilizing 14.0 grams of resinate containing 1.68 grams of platinum, 10.0 grams of gilsonite, 250 grams of benzene, and 50 grams of toluene. To a portion of this platinum solution was added, for convenience of this particular coating operation, an equal weight of additional benzene. A mass of the crushed screened particles of grade FC-36 graphite weighing 15.22 grams was coated with an excess of the resulting thinned solution and alowed to drain, leaving 2.0 grams of the solution containing 5.2 mg platinum. After drying at room temperature, the coated graphite was heated to remove the volatile and nonvolatile solvents and decompose remaining organic material, leaving 340 ppm elemental platinum disseminated on the surface of the particles, and then further heated at 600°C for 3 hours to obtain a mass of particles of dull, dark appearance. The resulting particles weighed 7.15 grams, corresponding to a weight loss of 53.0%. This same particulate material had a greatly increased surface area of 9.0 m^2/g. Another test of the particles having a surface area of 0.4 m^2/g was made by coating likewise with the same solution to obtain a platinum loading of 340 ppm, followed by the heating step with access of oxygen for 2.5 hours at 550°C. Under these treatment conditions the weight loss was only 8.3%, and the measured surface area was 5.7 m^2/g. This test has been listed for comparison in Table II as run No. 38, while the results obtained by heating the platinum-bearing particles for 3 hours at 600°C are included as run No. 39 in Table II.

Of these two runs, the run No. 38 carried out for 2.5 hours with a heating temperature of 550°C may be compared with runs Nos. 27 and 28. The run No. 39 in which heating was continued for 3 hours at 600°C resulted in a weight loss of slightly over 50% but provided a material of remarkably high surface area; this run may be compared with runs Nos. 34-36. It appears that the material obtained by crushing and screening the coherent grade FC-36 graphite material was somewhat more readily activated than BB-7, so that lower platinum loading or lower heating times and temperatures, or both, sufficed to obtain a given surface area with concomitant weight loss.

Example 7

If it is desired to use a coherent block or plate of graphite in a catalytic heater, it is important to determine that the molded graphite body has good heat stability, assuring dimensional integrity at the working temperatures of the heater which ordinarily are in the range of about 200° to 300°C, and further that no weight loss is encountered under such conditions. To confirm that the aforementioned grade FC-36 molded carbon blocks would provide the required stability, two smaller plates were machined from the massive blocks to obtain one plate, designated A, having dimensions of 62.2 × 49.0 × 6.1 mm and a weight of 31.39 grams, and another plate, designated B, of dimensions 60.9 × 49.0 × 6.1 mm and a weight of 30.78 grams. Plate A was treated with the platinum resinate solution of Example 1 by brushing onto the exposed surface 30.5 square centimeters in area on one side of the plate an amount of the platinum solution weighing 0.48 gram, resulting in a coating of 0.08 mg of elemental platinum per square centimeter of coated surface. Plate B was not treated with the platinum resinate solution. Both plates A and B then were placed in a furnace at 500°C, the furnace being continually purged with air to maintain oxidizing conditions. After 17 hours the graphite plates were removed from the furnace and weighed. The weight loss of plate A was only 2.9% and that of plate B without the platinum coating was even less, 1.8%. There was no distortion or any other observable damage to the plates. Since 500°C would be excessively high for the operating temperature of the catalytic heaters for which the activated graphite plates are to be used, this graphite material was considered to be suitable and of good stability.

Example 8

To provide a graphite plate for testing in a catalytic heater, another plate was machined from a massive block of grade FC-36 graphite to obtain dimensions of 2.75 × 2.75 × 0.25 inches (7.0 × 7.0 × 0.64 cm). A square portion, 2.375 inches (6.0 cm) on a side in the center of the plate, having an area of 5.64 square inches, was perforated by drilling 343 holes of

1/32 inch diameter in this area, with the holes spaced at equal distances, leaving an exposed treatment portion having an area of 5.4 square inches or 34.7 square centimeters. The weight of the perforated plate was 56.0 grams. It will be understood that the shape and dimensions of the plate were chosen simply for convenience of use in a catalytic burner demonstration.

The square exposed area on one side of the plate was treated as follows: platinum resinate-gilsonite solution in 250 grams of benzene and 50 grams of toluene, prepared as in Examples 1 and 6, was applied by brush onto one side of the 2.375-inch square perforated exposed area on the plate, dried for 15 minutes at 100°C, and the plate cooled. The coating, drying, and cooling was repeated, resulting in a total platinum metal loading of 140 mg, which is 250 ppm based on the weight of the plate, or more relevant, 0.40 milligram of platinum per square centimeter of coated surface, calculated from the weight of platinum resinate solution actually applied. It will be appreciated that the coating density in weight per unit area is based on the gross geometrical area coated, computed from the linear, planar, or apparent dimensions of the exposed regions to which the coating material is applied, and not on the B.E.T. surface area measured by adsorption techniques which takes into account microscopic surface irregularities or porosity. The plate thus coated then was oxidized for 3 hours at 600°C in an electric muffle furnace with the exposed coated surface facing upward and exposed to the air in the furnace. After 3 hours the weight loss was 4.1% for the entire plate of 6.4 mm thickness, which is equivalent to 26% of the weight of a surface portion of the plate 1 mm thick extending beneath the treated surface portion of the plate. Due to the treatment the coated exposed surface had changed from a shiny appearance to a dull, black color, indicating etching of the surface and activation with creation of porosity and enhanced effective area at the surface of the plate.

The above-mentioned weight of 0.40 mg platinum per square centimeter, deposited on the exposed surface of the plate for activation by heating, can be decreased very substantially, e.g. to about 0.02 mg, or less, of platinum per square centimeter of exposed surface (computed from the linear or apparent dimensions of the coated regions). This is demonstrated by the facility with which the heating treatment was accomplished to obtain high surface area values in the runs reported in Example 6 for the same material reduced to particulate form and coated with 340 ppm platinum. For particle sizes in the general size range of the parricles used in the tests of Example 6, having particle diameters of the order of 2 mm, the total loading of the surfaces of such particles, when carrying a weight of 75 ppm platinum (based on total original weight of the particles), is roughly equivalent to a platinum loading, when determined as weight per unit surface area, of 0.004 mg per square centimeter of apparent or geometric surface area. Thus at least about 0.004 mg of platinum per square centimeter should be used for the activating treatment.

Likewise the heating should be carried out for a sufficient time and at a sufficiently high temperature to give a weight loss of at least 3%, and preferably from 6% up to 25%, or up to 40% or even higher. Such a high loss can be tolerated when using a massive block or plate of high mechanical strength which, after such treatment, will function as a catalyst for an extended period of use. The percentage weight loss is based on the original weight of the activated surface portion of the body which is taken as extending 1 mm below the treated exposed surface. A depth of 1 mm is used for the computation of weight loss not only for convenience of computation, but also to indicate that a commensurate effective surface area, and hence utility as a catalyst substrate, is obtained. The weight loss may be expressed for particulate graphite as the percentage of total weight of the particles, and may be expressed for a graphite surface as a percentage of the weight of an exposed surface layer of a specified thickness; thus when the thickness of such surface portion of a block or plate is taken as 1 mm, the effective surface areas are roughly equivalent for a given weight loss value, assuming treatment with equivalent platinum loadings and heating times and temperatures. It may be possible to estimate the surface area of a plate by cutting out a small section of the plate including a part of the activated surface, and exposing only that part of the surface for the B.E.T. surface area measurement, taking as the weight basis the weight of a 1 mm thickness of the plate underlying the measured part of the surface. The surface area of the activated plate surfaces also may be confirmed approximately by scraping off a surface layer to a depth of about 1 mm or somewhat less and performing a B.E.T. surface area measurement on the resulting particles.

Example 9

This example illustrates the preparation of a catalyst plate using as substrate the plate having a treated or activated surfaces portion with perforations therethrough and thereunder, as prepared in Example 8. More of the platinum resinate in a mixture of essential oils, but without the gilsonite and the volatile solvents, was brushed on the treated surface, and the plate again heated in a mechanical convection oven for 30 minutes at 300°C.

After cooling, an additional coat of the same resinate was applied, followed by the same cycle of heating and cooling. After this further coating, the calculated loading with platinum was 1900 ppm based on the weight of the graphite plate or, more specifically, 2.9 mg of platinum per square centimeter of treated and coated surface.

As indicated hereinabove, a variety of catalyst materials along with procedures for their application, is available for incorporating to the activated surfaces of a mass of graphite, prepared in accordance with a feature of the present invention to provide a finished catalyst of usefully high surface area. Such a catalyst thus may be useful in a great variety of catalytic reactions, such as oxidation, reduction in hydrogenation, alkylation and halogenation, especially when the reaction is carried out in a corrosive medium to which the graphite is highly resistant, for example in media which are too alkaline or too acidic to be withstood by alumina and other conventonal catalyst supports. For use by way of example in catalytic oxidation generally and more specifically for oxidizing a carbonaceous material by contacting the material in fluid form under oxidizing conditions with a catalyst, as for instance in the oxidation of ethylene or propylene to the respective oxide or in the burning of fuels, various other catalytically active materials may be substituted for the materials illustrated by way of example in Examples 3-5 and 9. Thus any of the noble or precious metals, or mixtures or alloys thereof, may be applied and incorporated to the activated graphite surfaces, notably the platinum group metals and preferably platinum or palladium or mixtures thereof as well as gold or silver. Of the base metals, it is known in the art of catalysis that useful catalytic efficacy may be obtained for various reactions with a catalytically active metal, notably one of the nonprecious transisition metals having two oxidation states. Those elements having atomic numbers 22-31, 40-49, and 72-81 inclusive may be classified as the transition metals. Among the useful examples of such catalytically active base metals may be mentioned vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, tungsten, and rhenium; selenium, tin, and cerium, also are known for catalytic activity. Mixtures and alloys of these base metals, such as nickel-chromium or cobalt-chromium, have been found useful. Under operating conditions a base metal or metals may be present as a compound, such as a salt and frequently as the oxide, or as a mixture of base metal compounds or oxides which may take the form of a mixed oxide compound.

Thus catalysts may be prepared, for example, by the procedures of Examples 3 and 9 using catalytically effective amounts of a material selected from the group of precious metals and base metals as just discussed, and using more particularly at least one platinum group metal, notably platinum itself. The utility of such catalysts for oxidation as carried out in the flameless catalytic combustion of natural gas, gaseous alkanes, and other gaseous fuel-air mixtures has been demonstrated by preparing two catalytic burners as shown in Figures 1 and 2.

Referring first to Figure 1, the catalytic burner there shown comprises a conical steel cup having a gas inlet passage 11 at its apex. The cup is filled partially full, to a depth of about 80% of its height, with an inactive granular graphite material or other suitable pervious filler material 12. A 40-mesh per inch steel screen 13 is placed on top of the filler material, and the remainder of the cup is filled with catalytically active particulate material 14. Gas to be burned, which may be premixed with combustion air, is fed to the cup through a flexible inlet bore 15 connected to the inlet passage 11.

Referring now to Figure 2, there is shown a modified form of catalytic burner. This burner comprises a holder 20 formed of fire brick or other suitable refractory material. The upper portion of the holder defines a chamber 21 in which is placed a bottom layer of silica glass wool 22, above which the chamber is filled with ceramic spheres 23. The top rim of the holder is recessed to provide a support shoulder 24, on which is supported a perforated graphite catalyst plate 25. Gas to be burned, preferably premixed with an excess of combustion air, is fed to the holder chamber through a passage 26 and gas inlet tube 27. The holder may be either square or of other cross-sectional shape.

Example 10

A granular platinum-graphite catalyst, produced in accordance with Example 3, was applied in an amount of 28.3 grams, in a layer 9.5 mm thick and on the average about 8 particles deep, to provide the material 14 in the burner shown in Figure 1. Natural gas, having a composition by volume of methane, 82%; ethane, 5%; hydrogen, 4%; nitrogen, 2%; and the balance composed of saturated and unsaturated gaseous hydrocarbons and and inorganic gases, was fed to the burner, the gas ignited, and the fixture allowed to be heated up to about 200°-300°C by the flame. The gas flow was then slowly decreased to 32 liters per hour, resulting in a dying of the flame and catalytic combustion of the natural gas in weak admixture with ambient air flowing to the burner by natural convection. At steady state the temperature above the granules was about 180°C. The experiment was run for 60 hours and

then discontinued.

Example 11

It will be appreciated that gaseous fuels, typicaly the lower alkanes and more generally a fuel selected from the group consisting of the lower alkanes, carbon monoxide, and hydrogen, may be combusted in a burner utilizing the activated granular graphite catalyst, usually with access of, or premixing with, an amount of air well in excess of the stoichiometric amount so as to produce low catalyst temperatures and low effluent gas temperatures. Thus, an experiment similar to that described in Example 10 was carried out in the same apparatus using methane gas from cylinders as the fuel. At a methane flow of 32 liters per hour, a steady-state surface temperature of 180°C again was measured and the run discontinued after 60 hours. Using the same burner apparatus but with n-butane as the gas feed, a steady-state surface temperature of 180°C was obtained at a flow of 4.2 liters of butane per hour. Likewise, propane, or commercial propane containing some butylene, may be burned in place of the butane at quite low temperatures.

Using the same burner and carbon monoxide as gas feed, the steady-state surface temperature was 200° to 220°C at a flow of 17 liters of carbon monoxide per hour.

Another experiment was done using a premixed fuel feed to the inlet 15 of 80% natural gas and 20% air by volume. A steady-state temperature of 180°C was again measured at a flow of 36 liters/hour.

Example 12

In another experiment a burner of a configuration similar to that shown in Figure 1 was used after applying 11.3 grams of the 0.88% Pt-graphite catalyst of Example 3 in a circular bed 8 mm high and 52 mm in diameter. A mixture of 93% nitrogen and 7% hydrogen by volume was used. At a gas flow of 240 liters per hour a steady-state temperature of 110°C was observed. This hydrogen-containing gas mixture exhibited the advantageous characteristic that no preheating of the bed or initial lighting of a flame was necessary. To demonstrate this automatic, cold-start activity, the entire burner cup was cooled to 10°C and the experiment repeated. The surface temperature increased to 106°C in 15 minutes and then remained steady.

Hydrogen-containing gas mixtures such as that used in this experiment have significant industrial applications and are produced readily in commercially available generators, known for example as "Nitroneal" generators (Engelhard Industries, Newark, New Jersey) or as "Atmosphere generators" (Sunbeam Company, Meadville, Pennsylvania). Such gases are known under the name of "annealing gas" or "forming gas" and are prepared by partial combustion of ammonia gas or natural gas with controlled amounts of air. Depending on the amount of air used in the partial combustion, the hydrogen content can be regulated at between 0.5% and 25% by volume, the main component being nitrogen and the gas also containing smaller amounts of carbon monoxide and carbon dioxide.

A similar experiment was done using an inlet gas mixture of 14% propane and 86% air by volume. At a flow rate of 170 liters per hour a steady-state temperature of 260°C was observed.

Example 13

A platinized perforated graphite plate, formed as described in Example 9, was mounted in a fire-brick fixture as shown in Figure 2 with the treated surface of the plate facing upward and exposed to the air. Butane was fed to the heater at a flow of 11 liters per hour and passed upwardly through the perforations in the plate to its upper surface. Catalytic oxidation of the butane occurred at the treated surface of the plate carrying platinum at high effective surface areas. A steady-state upper surface temperature of 225°C was measured and the experiment discontinued after 8 hours. It will be understood that, for the desired fuel feed rates, the plate configuration is designed with the perforations spaced so as to permit access of combustion air while burning occurs over most of the plate surface area. At higher rates of fuel flow it would be desirable to mix some air with the fuel feed to insure complete combustion and to obtain the desired plate temperature, or it might be desirable to modify the layout of the perforations, or both. Alternatively, an imperforate treated plate may be used with means (not shown) for guiding the fuel-air mixture from one edge of the plate closely past the treated catalytically active surface, the effluent then leaving at the opposite edge of the plate.

WHAT WE CLAIM IS:-

1. A method of activating inactive graphite having a surface area of less than 1 m^2/g which comprises: contacting and wetting graphite having an ash content of less than 2% by weight with an organic solution of a platinum compound to deposit on the surface exposed to the solution, an amount of the solution containing at least 0.004 mg of elemental

platinum per square centimeter of surface:

heating the wetted graphite with access to oxygen to remove organic solvent and decompose the platinum compound. heaving elemental platinum disseminated on the graphite surface. heating being continued for a period of time sufficient to effect a weight loss of at least 3%. based on the weight of graphite, referred, when the graphite is- in the form of a coherent or shaped body. to the weight of graphite extending 1 mm below the activated exposed surface.

2. A method as claimed in Claim 1. wherein heating is effected at a temperature of 500° to 800°C.

3. A method as claimed in Claim 1 or 2 wherein said heating is continued for a period of time sufficient to effect a weight loss of between 6 and 25%, based on the weight of the portions of said body extending 1 mm below said exposed surfaces.

4. A method as claimed in any of Claims 1 to 3, wherein said soluble platinum compound is a platinum resinate.

5. A method as claimed in any of Claims 1 to 3, wherein said soluble platinum compound is a halogenoplatinous mercaptide-sulfide complex.

6. A method as claimed in any preceding Claim wherein the activated surfaces of said graphite are impregnated after said heating with a catalyst material.

7. A method as claimed in Claim 6. wherein said catalyst material applied on to said activated graphite is a precious metal. a mixture or alloy of a precious metal, a base metal selected from iron. cobalt. nickel. vanadium. chromium. manganese, copper, selenium, molybdenum. tin. cerium. tungsten. and rhenium, a mixture or alloy of said base metals, a compound of said base metal. or a mixture thereof.

8. A method as claimed in Claim 6 wherein the catalyst material applied on to said activated graphite is a platinum group metal.

9. A method as claimed in any preceding Claim wherein the graphite is a coherent body.

10. A method as claimed in any of Claims 1 to 8 wherein the graphite comprises a mass of particles, which are contacted with the solution of soluble platinum compound to deposit on the surfaces at least 75 ppm of elemental platinum.

11. A method as claimed in Claim 10. wherein said particles have diameters predominantly in the range of 1 to 5 mm.

12. A method as claimed in Claim 10 or 11, wherein the amount of said solution deposited on the surfaces of the particles contains between 75 and 2000 ppm of elemental platinum. based on the weight of said particles.

13. A method as claimed in any of Claims 10 to 12. wherein heating of said particles is continued for a period of time sufficient to effect an increase in particle surface area to at least 3 m^2 per gram.

14. A method as claimed in Claim 13. wherein the graphite particles lose between 3 and 40% of their weight during said heating.

15. A method as claimed in claim 13 wherein graphite particles lose at least 10% of their weight during said heating. and have a surface area of at least 6 m^2 per gram.

16. A method as claimed in any of Claims 10 to 15, as dependent upon Claim 8, wherein the impregnation of said particles after heating with at least one platinum group metal, is carried out to provide a catalyst containing at least 0.5% platinum by weight and having a surface area of at least 3 m^2 per gram.

17. An activated graphite mass produced by a process as claimed in any of the preceding Claims.

18. A catalyst composition which comprises an activated graphite mass impregnated with a catalyst material obtained by a method as claimed in any of Claims 6 to 16.

19. A mass of graphite as claimed in Claim 17. wherein said graphite comprises a particulate mass. the particles of which have said activated surfaces.

20. A mass of graphite as claimed in Claim 19 having a surface area of at least 3 m^2 per gram. and having disseminated on the particles thereof between 75 and 2000 ppm of elemental platinum. based on the weight of said particles.

21. A mass of graphite as claimed in Claims 19 or 20. in which the particles have diameters predominantly in the range of 1 mm to 5 mm.

22. A mass of graphite as claimed in Claim 17 and substantially as hereinbefore described with reference to any of the Examples.

23. A catalyst composition comprising a mass of graphite as claimed in any of Claims 17 and 19 to 22. impregnated with a catalyst material.

24. A method for oxidizing a carbonaceous material which comprises contacting said material in fluid form under oxidizing conditions with a catalyst composition as claimed in Claim 18 or 23.

25. A method as claimed in claim 24 which comprises combusting a gaseous fuel-air

mixture.

26. A method as claimed in Claim 25, wherein the gaseous fuel in said fuel-air mixture is a lower alkane, carbon monoxide, or hydrogen.

27. A method as claimed in Claim 24 and substantially as hereinbefore described with reference to any of Examples 10 to 13.

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1601715 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

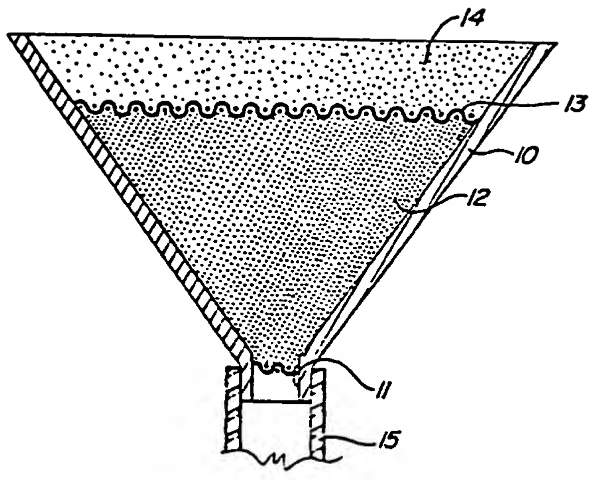

Fig - 1

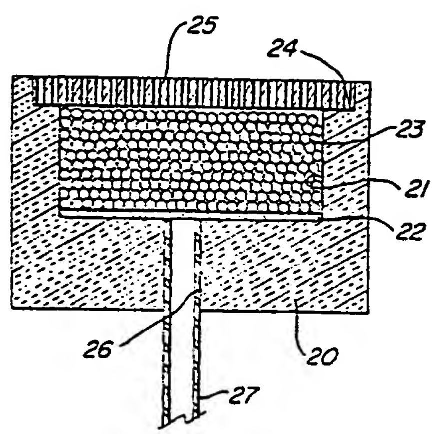

Fig - 2